Methane Hydrates and Contemporary Climate Change

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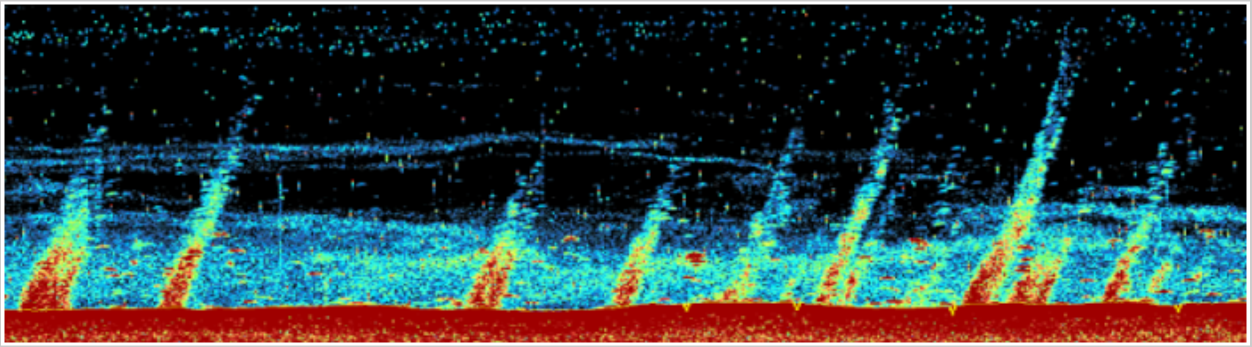

As the evidence for warming climate became better established in the latter part of the 20th century (IPCC 2001), some scientists raised the alarm that large quantities of methane (CH_4) might be liberated by widespread destabilization of climate-sensitive gas hydrate deposits trapped in marine and permafrost-associated sediments (Bohannon 2008, Krey *et al*. 2009, Mascarelli 2009). Even if only a fraction of the liberated CH_4 were to reach the atmosphere, the potency of CH_4 as a greenhouse gas (GHG) and the persistence of its oxidative product (CO_2) heightened concerns that gas hydrate dissociation could represent a slow tipping point (Archer *et al*. 2009) for Earth's contemporary period of climate change.

Methane Hydrate Primer

Methane hydrate is an ice-like substance formed when CH4 and water combine at low temperature (up to ~25°C) and moderate pressure (greater than 3-5 MPa, which corresponds to combined water and sediment depths of 300 to 500 m). Globally, an estimated 99% of **gas hydrates** occurs in the sediments of marine continental margins at **saturations** as high as 20% to 80% in some lithologies; the remaining 1% is mostly associated with sediments in and beneath areas of high-latitude, continuous permafrost (McIver 1981, Collett *et al*. 2009). Nominally, methane hydrate concentrates CH_4 by ~164 times on a volumetric basis compared to gas at standard pressure and temperature. Warming a small volume of gas hydrate could thus liberate large volumes of gas.

A challenge for assessing the impact of contemporary climate change on methane hydrates is continued uncertainty about the size of the global gas hydrate inventory and the portion of the inventory that is susceptible to climate warming. This paper addresses the latter issue, while the former remains under active debate. Dickens (2011) recently estimated $7x10^2$ to $1.27x10^4$ Gt carbon (Gt C) to be sequestered in marine gas hydrates alone, while Shakhova *et al.* (2010a) estimate $3.75x10^2$ Gt C in methane hydrates just on the East Siberian Arctic shelf (ESAS). A conservative estimate (Boswell & Collett 2011) for the global gas hydrate inventory is ~$1.8x10^3$ Gt C, corresponding to CH4 volume of ~$3.0x10^{15}$ m3 if CH_4 density is taken as 0.717 kg/m^3. In the unlikely event that 0.1% (1.8 Gt C) of this CH_4 were instantaneously released to the atmosphere, CH_4 concentrations would increase to ~2900 ppb from the 2005 value of ~1774 ppb (IPCC 2007).

Why Methane Matters

Concern about the long-term stability of global gas hydrate deposits is rooted in the potential impact that a large CH_4 release might have on global climate. CH_4 is ~20 times more potent than CO_2 as a GHG, but it oxidizes to CO_2 after about a decade in the atmosphere. In recent models, the longer-lived CO_2 oxidation product (Archer *et al.* 2009), not the CH_4 itself (e.g., Harvey & Huang 1992), is credited with causing most of the excess atmospheric warming that would follow large-scale **dissociation** of methane hydrates.

The present-day concentration of CH_4 in the atmosphere is ~200 times lower than that of CO_2, but CH_4 concentrations have risen by ~150% since pre-industrial times, compared to only ~40% for CO_2 (IPCC 2001). Rising atmospheric CH_4 concentrations lead to more rapid depletion of the hydroxyl radicals needed for oxidation, longer CH_4 residence times, and thus increased CH_4-induced warming (Lelieveld *et al.* 1998). Present-day CH_4 emissions are dominated by wetlands, ruminants, fossil fuel production, and rice cultivation (IPCC 2001), sources that fluctuate with season, human behavior, and other factors. The IPCC (2001, 2007) relies on estimates and models (Fung *et al.* 1991, Lelieveld *et al.* 1998, Wang *et al.* 2004) to attribute ~3.75×10^{-4} Gt C (IPCC 2001), or ~1% of annual global CH_4 emissions, to dissociating gas hydrates. This estimate has never been validated, nor do any observational data unequivocally link specific CH_4 emissions or regionally integrated CH_4 fluxes to dissociating gas hydrates. Against the backdrop of a well-mixed atmosphere, strong annual fluctuations, and a significant increase in CH_4 concentrations over the 20th century, detecting a CH_4 signal that is directly attributable to dissociating gas hydrates may always remain challenging.

Gas Hydrates and Past Warming Events

The geologic record is punctuated by warming events that may provide clues about future interactions between methane hydrates and climate change. The Paleocene-Eocene Thermal Maximum (PETM) at ~54.95 Ma is the most intensely studied of these **hyperthermals** (e.g., Dickens *et al.* 1995, Schmidt & Shindell 2003, Renssen *et al.* 2004, Zachos *et al.* 2001, 2005, Röhl *et al.* 2007). The large, negative **carbon isotopic excursion** (CIE) recorded in both marine and terrestrial sediments during the PETM has been interpreted as reflecting widespread release of isotopically-light (microbial) carbon from dissociating marine methane hydrates (e.g., Dickens *et al.* 1995, Zachos *et al.* 2005). This explanation is also invoked to explain CIEs in other deep-time warm periods (Hesselbo *et al.* 2000, Jiang *et al.* 2003). Negative CIEs also undergird the clathrate gun hypothesis (CGH), which postulates that repeated warming of intermediate ocean waters during the Late Quaternary (since 400 ka) triggered periodic dissociation events (Kennett *et al.* 2003).Ice core data (Sowers 2006) and geologic studies (Maslin *et al.* 2003) have challenged the CGH, while Bock *et al.* (2010) and Petrenko *et al.* (2009) question the role of gas hydrate dissociation in contributing to increased atmospheric CH_4 during more recent warming events as well. Northern hemisphere wetlands, which may experience increased production of isotopically-light CH_4 in response to local warming, appear to be the key culprit in enhancing atmospheric CH_4 concentrations during several Pleistocene (~2.6 Ma to 10 ka) and Holocene (since 10 ka) warming events.

Fate of Contemporary Methane Hydrates During Warming Climate

The susceptibility of gas hydrates to warming climate depends on the duration of the warming event, their depth beneath the seafloor or tundra surface, and the amount of warming required to heat sediments to the point of dissociating gas hydrates. A rudimentary estimate of the depth to which sediments are affected by an instantaneous, sustained temperature change DT in the overlying air or ocean waters can be made using the diffusive length scale $1 = \sqrt{kt}$, which describes the depth (m) that 0.5 DT will propagate in elapsed time t (s). k denotes thermal diffusivity, which ranges from ~0.6 to 1×10^{-6} m^2/s for unconsolidated sediments. Over 10, 100, and 1000 yr, the calculation yields maximum of 18 m, 56 m, and 178 m, respectively, regardless of the magnitude of D*T*. In real situations, D*T* is usually small and may have short- (e.g., seasonal) or long-term fluctuations that swamp the signal associated with climate warming trends. Even over 10^3 yr, only gas hydrates close to the seafloor and initially within a few degrees of the thermodynamic stability boundary might experience dissociation in response to reasonable rates of warming. As discussed below, less than 5% of the gas hydrate inventory may meet these criteria.

Even when gas hydrate dissociates, several factors mitigate the impact of the liberated CH4 on the sediment-ocean-atmosphere system. In marine sediments, the released CH_4 may dissolve in local pore waters, remain trapped as gas, or rise toward the seafloor as bubbles. Up to 90% or more of the CH_4 that reaches the **sulfate reduction zone** (SRZ) in the near-seafloor sediments may be consumed by anaerobic CH_4 oxidation (Hinrichs & Boetius 2002, Treude *et al*. 2003, Reeburgh 2007, Knittel & Boetius 2009). At the highest flux sites (seeps), the SRZ may vanish, allowing CH_4 to be injected directly into the water column or, in some cases, partially consumed by aerobic microbes (Niemann *et al*. 2006).

Methane emitted at the seafloor only rarely survives the trip through the water column to reach the atmosphere. At seafloor depths greater than ~100 m, O_2 and N_2 dissolved in ocean water almost completely replace CH_4 in rising bubbles (McGinnis *et al.* 2006). Within the water column, oxidation by aerobic microbes is an important sink for dissolved CH_4 over some depth ranges and at some locations (e.g., Mau *et al.* 2007). These oxidizing microbial communities are remarkably responsive to environmental changes, including variations in CH_4 concentrations. For example, rapid deepwater injection of large volumes of CH_4 led to dramatically increased oxidation in the northern Gulf of Mexico in 2010 (Kessler *et al.* 2011, Yvon-Lewis *et al.* 2011). Water column CH_4 oxidation mitigates the direct GHG impact of CH_4 that is emitted at the seafloor, but it also depletes water column O_2, acidifies ocean waters, and leads to the eventual release of the product CO_2 to the atmosphere after residence times (Liro *et al.* 1993) of <50 years (water depths up to 500 m) to several hundred years (more profound water depths).

Global Warming and Gas Hydrate Type Locales

Methane hydrates occur in five geographic settings (or sectors) that must be individually evaluated to determine their susceptibility to warming climate (Figure 1). The percentages assigned to each sector below assume that 99% of global gas hydrate is within the deepwater marine realm (McIver 1981, Collett *et al*. 2009). Future refinements of the global ratio of marine to permafrost-associated gas hydrates will require adjustment of the assigned percentages. Owing to the orders of magnitude uncertainty in the estimated volume of CH_4 trapped in global gas hydrate deposits, the percentages below have not been converted to Gt C.

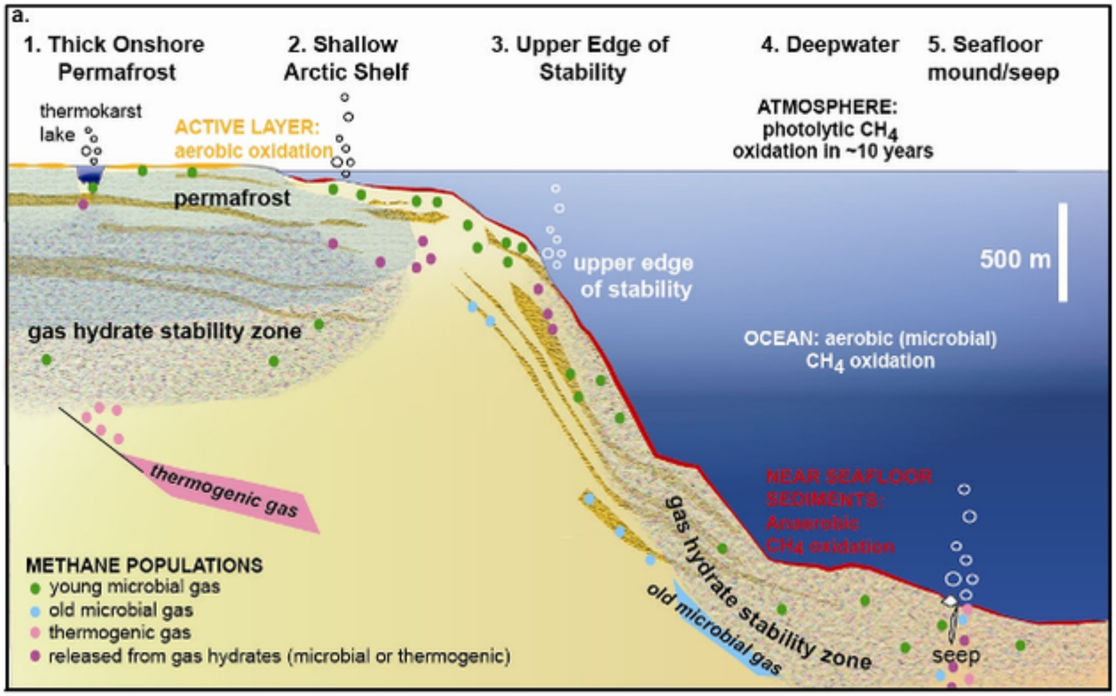

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Figure 1a: Gas hydrate sectors and their response to climate change.

Schematic cross-section from a high-latitude ocean margin (onshore permafrost and shallow offshore subsea permafrost) in Sectors 1 and 2 on the left, across a generic upper continental slope (Sector 3), and into a deepwater marine gas hydrate system (Sector 4) and an area of gas seeps on the right (Sector 5). The horizontal scale on Arctic Ocean margins may range from less than 10^2 to 10^3 km. GHSZ sediments usually have low saturations of methane hydrate, except in permeable sand layers shown here with coarser-grained texture. Ice-bonding within permafrost follows similar relationships. New microbial CH_4 (green) can be formed where labile organic carbon is available, including within the GHSZ, beneath lakes in permafrost areas, and in newly thawed sediments above subsea or terrestrial permafrost. Red zones at and below the seafloor denote anaerobic CH_4 oxidation (coinciding with sulfate reduction), which occurs in zones that thin with increasing CH_4 flux. The orange zone onshore denotes seasonal aerobic CH_4 oxidation in the annually thawed active layer. CH_4 oxidation associated with lakes in permafrost is not depicted. Methane, not necessarily derived from gas hydrates, is emitted directly to the atmosphere at ebullition sites in shallow lakes within permafrost and probably in open water on shallow Arctic shelves. Methane emitted at the seafloor at greater water depths is not likely to reach the atmosphere.

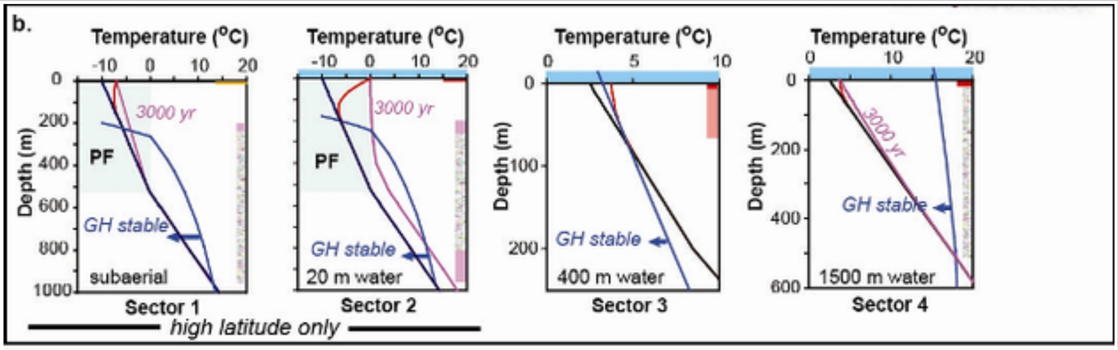

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Figure 1b: Gas hydrate sectors and their response to climate change.

The effects of climate warming on gas hydrates can be roughly estimated by comparing geotherms before and after warming events. The plots, which are on different depth and temperature scales, show the initial geotherm (black), the thermodynamic conditions for gas hydrate stability (blue) for pure CH_4 hydrate in equilibrium with freshwater (sectors 1 and 2) and nominal seawater (sectors 3 and 4), and the geotherms after 100 and 3000 yr of warming (red and purple) due to an instantaneous, sustained increase in temperatures DT at the surface (sector 1) or seafloor (sectors 2 to 4), assuming homogeneous, constant thermal diffusivity of 10^{-6} m^2/s. Changing CH4 solubility in pore waters and endothermic heat of gas hydrate dissociation are not considered. The light blue boxes for Sectors 1 and 2 denote permafrost, and the stippled column shows GHSZ thickness after 3000 yr of warming. The purple (Sectors 1 and 2) and pink (Sector 3) columns correspond to the dissociated portion of the GHSZ for 3000 yr and 100 yr temperature perturbations, respectively.

1. Thick (> 300 m) continuous permafrost onshore (<1%).

Deep gas hydrates beneath capping, permafrost-bearing sediments are stable over warm periods that endure more than 10^3 yr (e.g., Lachenbruch *et al*. 1994), even under scenarios of doubling atmospheric CO_2 (Majorowicz *et al*. 2008). Only gas hydrates at the top of the GHSZ, nominally at ~225 m depth for pure CH_4 hydrate within permafrost, might be vulnerable to dissociation due to atmospheric warming over 10^3 yr. Such shallow, intrapermafrost gas hydrate has been sampled in the North American Arctic (Collett *et al*. 2011, Dallimore & Collett 1995), but is not necessarily ubiquitous at high latitudes. Warming Arctic temperatures tracked in deep boreholes since the 1960s provide no evidence for climate perturbations reaching as deep as 200 m (Judge & Majorowicz 1992, Lachenbruch & Marshall 1986) in normal (e.g., not beneath lakes) continuous permafrost. Some researchers have argued that gas hydrates formed during previous periods of ice/water loading may persist today at subsurface depths as shallow as 20 m in areas of continuous permafrost (Chuvilin *et al*. 1998). Although their existence is controversial, such shallow gas hydrates would clearly be highly susceptible to dissociation in response to climate warming.

Simple numerical model: Adopting a pre-warming surface temperature of -10°C and initial geotherms of 19°C/km and 30°C/km within and beneath permafrost, respectively, sustained surface warming over 100 yr with *DT* =3°C at the surface does not raise temperatures enough to perturb the top of the GHSZ (Figure 1b). Warming over 3000 yr would lead to some thinning of permafrost and to dissociation of intrapermafrost gas hydrates in the shallowest part of the GHSZ.

Example: In the Mackenzie Delta, where permafrost is several hundreds of meters thick, Bowen *et al*. (2008) document seep gas composition similar to that of gas sequestered in nearby gas hydrates. There is no proof that active gas hydrate dissociation, as opposed to leakage of compositionallysimilar free gas, supplies these seeps or other CH_4 ebullition sites that occur throughout the Arctic region (e.g., Walter *et al.* 2007). Such sites should continue to be evaluated for evidence of a potential link to climate-driven gas hydrate dissociation.

2. Subsea permafrost on the circum-Arctic shelves (<0.25%?).

Sediments on shallow marine continental shelves that fringe the Arctic Ocean are often underlain by permafrost and associated gas hydrates that formed in Pleistocene time, when these regions were subaerial and exposed to much colder annual temperatures. Since the Late Pleistocene, marine inundation of these former coastal plains has led to large (up to 17°C; Shakhova *et al.* 2010) temperature increases, partial thawing of subsea permafrost (Rachold *et al.* 2007), and inferred dissociation of gas hydrates (Semiletov *et al.* 2004). Increasing pressures (~1 MPa for 100 m of sea level rise since ~15 ka) would have only marginally offset the impact of warming temperatures on the GHSZ. Assuming that (a) 25% of northern-latitude continuous permafrost may have been flooded by Arctic Ocean transgressions since the Late Pleistocene, (b) some of this gas hydrate has dissociated over the past 10 kyr, and (c) less than 1% of the present-day global gas hydrate inventory is associated with permafrost implies that only a fraction of 1% of the global inventory occurs in areas of subsea permafrost. This estimate deserves considerable scrutiny in the coming years. Shakhova *et al.* (2010a) calculate that gas hydrates on the ESAS should sequester 20% of the carbon (375 Gt C) of the 1.8×10^3 Gt C within the conservative global gas hydrate inventory estimate (Boswell & Collett 2011).

Simple numerical model: Using the same initial conditions as for the terrestrial permafrost in Sector 1, a sustained temperature increase of $DT = 10°C$ and an accompanying minor pressure increase are applied to mimic the impact of marine inundation of formerly subaerial permafrost to a water depth of 20 m (Figure 1b). After 100 yr, the temperature perturbation has propagated just to the top of gas hydrate stability. After 3000 yr, the permafrost has thawed, and gas hydrates located near the top and the base of the GHSZ are dissociating and releasing CH_4.

Example: Shakhova *et al.* (2010) document CH_4 supersaturation in shallow ESAS coastal waters above sediments containing degrading subsea permafrost and presumably dissociating gas hydrates. Studies are underway in similar settings on the Beaufort Sea inner shelf (e.g., Paull *et al.* 2011, Ruppel *et al.* 2010). A substantial fraction of CH_4 that is emitted at the seafloor on Arctic shelves may reach the atmosphere since bubble dissolution and aerobic oxidation should be limited in such shallow (~5 to 50 m) waters. The challenge lies in proving that at least some of the elevated CH_4 concentrations detected in these settings is attributable to dissociating gas hydrates rather than to other processes associated with CH_4 generation and/or migration.

3. Deepwater marine hydrates at the feather edge of GHSZ (~3.5%).

The deepwater marine hydrate system thins to vanishing at shallow water depths (usually < 500 m) on the upper continental slopes. Because the entire GHSZ lies near the seafloor, upper continental slopes are the most susceptible places on Earth for wholesale gas hydrate dissociation driven by warming of impinging intermediate ocean waters. A maximum 3.5% of the global gas hydrate inventory might occur in these vulnerable settings assuming that (a) appropriate temperature-depth conditions for over the formation of a thin GHSZ occur over $\sim 6 \times 10^5$ km^2 of the upper continental slopes; (b) the GHSZ (3% saturation) is 40-m-thick; (c) the SRZ is missing owing to high seepage rates; and (d) warming climate does not necessarily raise water temperatures everywhere (e.g., Biastoch *et al.* 2011). As upper continental slope gas hydrate dissociates, the upper edge of the GHSZ moves downslope, priming more near-seafloor gas hydrate for dissociation. Dissolution of CH_4

bubbles or oxidation of CH_4 in the water column should prevent most of the CH_4 that could be released from these gas hydrates from reaching the atmosphere immediately or in the form of CH_4.

Simple Numerical Model: With an initial thermal gradient of 30°C/km and original seafloor temperature of 2.5°C, 100 yr of sustained warming (*DT* =1.25°C) of the intermediate waters that impinge on the upper continental slope leads to complete dissociation of the gas hydrate zone, originally ~40 m thick (Figure 1b).

Example: At water depths of 150 to 400 m on the West Spitsbergen continental margin, widespread gas seepage may reflect gas hydrate dissociation caused by ~1°C of ocean warming over the last 30 years (Westbrook *et al.* 2009). The connection between dissociating gas hydrates and the methane plumes has yet to be fully established, but observations there, in the Barents Sea (Lammers *et al.* 1995), and on the Canadian Beaufort Sea slope (Paull *et al.* 2011) provide compelling circumstantial evidence.

4. Deepwater gas hydrates (~95.5%).

These gas hydrates, which constitute most of the global inventory, generally have low susceptibility to warming climate over time scales shorter than a millennium. The gas hydrates closest to the edge of thermodynamic stability lie deep within the sedimentary section and close to the base of the GHSZ. Sustained bottom water temperature increases lasting many 10^3 yr would be required to initiate warming, no less dissociation. Even if CH_4 is released from gas hydrate and is able to migrate toward the seafloor, some CH_4 may be trapped in newly formed gas hydrate (e.g., Reagan & Moridis 2008) and much will be consumed in the SRZ.

Simple Numerical Model: Using the same initial conditions as for Sector 3 and assuming an increase in bottom water temperature of *DT* =1.25°C, sustained warming over 100 and 3000 yr produces no dissociation of gas hydrate (Figure 1b).

5. Seafloor gas hydrate mounds (trace).

At some marine seeps, massive, relatively pure gas hydrate occurs in seafloor mounds (e.g., Gulf of Mexico; Macdonald *et al.* 1994) and in shallow subseafloor layers (e.g., Suess *et al.* 2001) or conduits. These mounds are shown schematically as deepwater phenomena in Figure 1a, but in fact often occur at upper continental slope depths. While seafloor gas hydrate mounds and shallow subseafloor gas hydrates constitute only a trace component of the global gas hydrate inventory, they can dissociate rapidly due to expulsion of warm fluids from the seafloor (e.g., Macdonald *et al.* 2005), warming of overlying waters (e.g., Macdonald *et al.* 1994), or possibly pressure perturbations (Tryon *et al.* 2002). Direct measurements of CH_4 have alternately confirmed (Solomon *et al.* 2009) and challenged (Hu *et al.* 2011) the contention that significant CH_4 reaches the atmosphere due to gas hydrate dissociation at such seeps.

Conclusions

Catastrophic, widespread dissociation of methane gas hydrates will not be triggered by continued climate warming at contemporary rates (0.2°C per decade; IPCC 2007) over timescales of a few hundred years. Most of Earth's gas hydrates occur at low saturations and in sediments at such great depths below the seafloor or onshore permafrost that they will barely be affected by warming over even 10^3 yr. Even when CH_4 is liberated from gas hydrates, oxidative and physical processes may greatly reduce the amount that reaches the atmosphere as CH_4. The CO_2 produced by oxidation of CH_4 released from dissociating gas hydrates will likely have a greater impact on the Earth system (e.g., on ocean chemistry and atmospheric CO_2 concentrations; Archer *et al*. 2009) than will the CH_4 that remains after passing through various sinks.

Contemporary and future gas hydrate degradation will occur primarily on the circum-Arctic Ocean continental shelves (Sector 2; Macdonald 1990, Lachenbruch *et al*. 1994, Maslin 2010), where subsea permafrost thawing and methane hydrate dissociation have been triggered by warming and inundation since Late Pleistocene time, and at the feather edge of the GHSZ on upper continental slopes (Sector 3), where the zone's full thickness can dissociate rapidly due to modest warming of intermediate waters. More CH_4 may be sequestered in upper continental slope gas hydrates than in those associated with subsea permafrost; however, CH_4 that reaches the seafloor from dissociating Arctic Ocean shelf gas hydrates is much more likely to enter the atmosphere rapidly and as CH_4, not CO_2. Proof is still lacking that gas hydrate dissociation currently contributes to seepage from upper continental slopes or to elevated seawater CH_4 concentrations on circum-Arctic Ocean shelves. An even greater challenge for the future is determining the contribution of global gas hydrate dissociation to contemporary and future atmospheric CH_4 concentrations.

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Glossary

Carbon isotopic excursion (CIE): Climate scientists use isotopic signatures recorded in ice cores, deep ocean sediments, thick carbonate sequences, and other types of samples to reconstruct Earth's climate history and the composition of the ocean/atmosphere. ^{13}C isotopic signatures are commonly expressed as a $\delta^{13}C$ value. Deviations from the baseline $\delta^{13}C$ value are termed carbon isotopic excursions. Negative deviations in $\delta^{13}C$ of even 1 part per mille (written as 1‰) are substantial for records constructed from benthic and planktonic foraminifera tests. Such deviations imply the emission of large amounts of isotopically-light carbon (strongly negative $\delta^{13}C$ ratio) that likely originated through microbial methanogenesis. Large, climate-sensitive sources for isotopically-light methane carbon in the Earth system include wetlands and most natural gas hydrates.

Dissociation: The breakdown of gas hydrate occurs by dissociation to its constituent water and gas.

Gas hydrate: Gas hydrate is an ice-like solid that forms in sediments and remains stable at certain pressure-temperature conditions. Gas hydrates have a clathrate structure: water molecules form linked cages that enclose individual molecules of low molecular weight gas (e.g., CH_4, CO_2, hydrogen sulfide, ethane). Some water cages may be empty, rendering gas hydrates non-stoichiometric compounds and making it difficult to predict exactly how much gas will be released for dissociation of a given volume of gas hydrate. Gas hydrates in nature contain mostly methane as the trapped gas. This methane can originate from the microbial degradation of organic carbon or from deep burial and heating of organic matter, a so-called thermogenic process similar to that responsible for oil generation. Outside of hydrocarbon provinces, gas hydrate typically contains almost exclusively microbial methane.

Hyperthermals: Periods characterized by extremely warm climate conditions.

Saturation: The percentage of sediment pore space occupied by gas hydrate.

Sulfate reduction zone (SRZ): A zone within the marine sedimentary section starting at the sediment-water interface and extending downward to the depth at which sulfate is depleted as a result of the microbially-mediated oxidation of methane and other organic compounds. The thickness of the SRZ varies from centimeters to tens of meters and is inversely related to the upward flux of methane toward the seafloor and the organic matter content of the sediments. Most of the methane that enters the SRZ from below is consumed before it reaches the seafloor.

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